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FUEL CELL RESEARCH

An Investigation of Non-Steady-State Operation

CR-52890

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OUTLINE OF PROGRAM

The present program, covering a phased three-year period, relates to the study of fuel cell performance under non-equilibrium conditions, specifically to study the operation under pulsed loading with varying off-load periods to provide data in the following general areas.

1. The detailed aspects of electrode processes at electrodes operated under non-steady-state conditions.
2. A study of the non-equilibrium kinetics of reactions occurring at fuel cell electrodes.
3. The nature of electrolyte behavior (transport phenomena and polarization) under non-steady-state operation.
4. A feasibility study for the technological application of fuel cells operating under interrupted load for high-performance output.

Since there exists a considerable volume of data relating to the hydrogen-oxygen fuel cell, preliminary investigations are being addressed to the determination of the fundamental aspects of interruption loading of such cells, particularly in the determination of the nature of the electrode process and the extent to which this controls the duty cycle permissible. To this end a technique has been developed to ensure a high degree of reproducibility in assembling and operating cells for this program. During the course of this investigation, it should be possible to determine the feasibility of the application of this technique to improve power generators by which interrupted d.c. can be advantageously obtained and transformed to any requisite potential. It is visualized that several cells operating sequentially to produce multi-phase output would be employed in such service. This has the further advantage of eliminating the mechanical and electrical complication of series operation of individual fuel cell units.

From a fundamental point of view, it is important to determine the maximum pulse duration and load before which significant concentration polarization develops. In a suitable circuit which has now been developed under this program with an auxiliary grid electrode it should be possible to determine the time constant for the development of a specific thickness of polarization layer and equally the time constant of its disappearance under both static and dynamic conditions. This is of the utmost importance since at the present time the effect of concentration polarization is commonly expressed in terms of the diffusion constant, transport number and thickness of polarization layer determined from independent experiments and erroneously assumed constant under varying conditions of load. The effect of this polarization layer on the effective internal impedance of the cell is of the utmost importance and will be measured separately by a.c. Kelvin bridge.

At a later stage in the investigation, provision will be made for the incorporation of a piezoelectric device either in the electrode assembly or in the electrolyte connected to a suitable ringing circuit to facilitate the destruction of the concentration polarization layer during the off-cycle period. It is feasible that additionally a small reverse potential applied to the electrode may also be of assistance.

Based on the observations and experience derived from these preliminary studies, an attempt will be made to determine the intimate nature of the non-equilibrium reaction kinetics obtaining in fuel cells of various types under load conditions. Material balance will be investigated and the kinetics of the catalyzed electrode reaction studied.

This data will be correlated with information available from College and AFAPL supported fuel cell programs and through the Graduate Programs in Materials and Catalysis. Full analytical surveys of electrode and electrolyte constitution will be undertaken and data developed more specifically from the point of view of advancing fundamental knowledge and establishing the feasibility of predicting optimum operational conditions for a particular type of fuel cell.

INTRODUCTION

In the generalized consideration of fuel cell operation, it is conventional to relate the emf of the ideal fuel cell to the free energy decrease during the full cell reaction. Unfortunately, this relationship applies only under equilibrium conditions, essentially at open circuit, and does not provide a realistic approach to cell operation under medium to heavy load conditions. When operating in this manner, instead of the usual equilibrium thermodynamics, steady-state considerations should be applied using an Onsager method of analysis. It is entirely unjustifiable to expect accurate prediction of fuel cell operation under load when this is overlooked. Furthermore, the operation of the fuel cell under anything but open-circuit conditions involves a detailed appreciation of the electrochemistry of the overall assembly, complicated by electrode and concentration polarization which almost inevitably occurs when the cell is subjected to any extensive loading. The nature of the transport phenomena has been assumed in virtually all cases so far investigated rather than being studied and identified so that the selection and operation of electrolytes must be regarded as essentially empirical.

In considering the detailed fundamental investigation of fuel cell operation, the following points require specific attention. For any particular fuel and oxidant, an accurate knowledge of the reaction kinetics in a catalyzed electrode is essential. Much of this data is already available although not always in a form which can be directly applied to fuel cell operation. The correlation between defect solid state and catalysis, initiated at Bristol University, England, and subsequently developed here at Alfred and elsewhere, materially aids in the selection of suitable catalyst-electrode systems propitious for the desired reaction kinetics. It will be shown in this report that galvanostatic measurements are capable of adding very materially to detailed knowledge of the catalytic process at electrode/electrolyte interfaces. However, although important, this in itself is only one aspect of the electrode design since it is also necessary to provide a high conductivity path to the external circuit and also to so develop the electrode to minimize the effect of wetting and contamination by both electrolyte and reaction products. The latter can be most serious in the case of prolonged operation of a cell under heavy load conditions where the formation of polymer or carbon is detrimental.

The electrolyte commonly adopted for low-temperature operation has been caustic potash in the concentration range 20% to 30%. It has been demonstrated at Alfred, however, that carbonate electrolytes are equally suitable. Other electrolytes which have been satisfactorily employed are acid phosphate and salts of organic acids in aqueous media. These have also been operated as molten salts in the temperature range 150° to 250°C. Further detailed information is required to determine their individual characteristics. Very little accurate data is so far available

regarding the exact electrochemical operation of the electrolytes under conditions of high current density. Preliminary measurements have been made at Alfred using an auxiliary electrode by which means the function of the individual electrodes under varying electrolyte conditions can be investigated in considerable detail under open-circuit and load conditions. A wealth of most valuable data can be derived by this means if the load is applied both as a steady loading and as an interrupted pulse. Under the former condition, concentration polarization and electrode polarization both appear and modify the cell's operation while under the latter operating conditions, the concentration polarization is limited, if not eliminated. When these data are correlated with the a.c. impedance of the cell under load conditions, an exact analysis of operating characteristics can be achieved from which advantageous modifications may readily be predicted. A knowledge of these characteristics over a reasonable range of temperature will lead to a concise appreciation of the fundamental significance of electrolyte operation. It has already been established that this approach can facilitate modification to electrodes to optimize the output from a particular fuel cell.

In various endeavors to separate the individual functions of concentration polarization, electrode polarization, and conductivity effects, various interrupter techniques have been employed in chemical investigations over more than three decades. The original work of Stern¹ employed mechanical interrupters, but in 1937 Hickling² introduced a technique

¹Stern, O., Z. Elektrochem., 30, 508 (1924).

²Hickling, A., Trans. Faraday Soc., 33, 1540 (1937).

using thyratrons. This technique has been used extensively since that time, and was used by Gray in investigations of electrode overvoltage at Bristol in the period 1946-1954.

All of these techniques were essentially square wave interrupters and have been developed to a high degree of precision. They have some disadvantages, however, and are complicated in operation. More recently, Kordes and Marko³ introduced a simple interrupter operating in the frequency range 30 to 400 cycles per second based on the blocking of a silicon rectifier operating with sinusoidal input voltage. The equipment is eminently simple but does suffer from some severe limitations, the principal one being that the pulse duration and pulse repetition frequency are directly related and cannot be independently varied.

It has been established by work at Alfred that the application of ultrasonic vibration either to the fuel cell as a whole or to an individual electrode also assists in breaking down any polarization layer. This can be facilitated in the case of a pulse loaded cell by a simple ringing circuit and transducer operating from an inductive kick developed when the load is removed.

When the electrode kinetics and electrolyte significance for a particular system are reasonably understood, a further feature becomes important. If complete combustion of the entire fuel feed is undertaken in a single cell, contamination of the electrode will almost inevitably be serious. Experience in many laboratories, particularly by Chambers at Soudes Place Research Laboratories, indicates that reaction in an individual unit must be restricted to about 25% in order that no excessive buildup of product occurs. The tandem operation of several units

³Kordes, K. and Marko, J. Electrochem. Soc., 107, 380 (1960).

(usually 3 to 4) gives overall combustion efficiencies of 70 to 75%. This will be investigated at a later stage in respect to hydrocarbon fuel cells for which the galvanostatic measurement technique has already been demonstrated as providing valuable preliminary data.

An important aspect of fuel cells so far overlooked is the feasibility of using them as a unique method for the fundamental study of non-equilibrium reaction kinetics. It is extremely difficult to study such processes accurately by conventional techniques; however, using a fuel cell operating under load, it is possible by a detailed study of material balance, electrical output and thermal characteristics, to achieve a very exact study of non-equilibrium kinetics. Not only is this of itself of considerable importance, but for the further development of fuel cells and for the assessment of their future potentiality such information is imperative. In conjunction with the recently developed precision galvanostatic techniques developed at Alfred, this unique approach should provide information of profound importance for a wide variety of catalytic processes.

Without fundamental data based on these various considerations, the further development of fuel cells can only be regarded as problematical. An empirical approach can, in some cases, be justified but the present status of fuel cells strongly suggests that basic fundamental data is imperative and the above outline suggests the most rational and direct approach.

EXPERIMENTAL

Pulse Loading System

In the initial stages of this program, attempts were made to obtain satisfactory pulsed loading of fuel cells with varying duty cycle by the use of a dual electronic timing circuit driving either a mechanical or a mercury relay as a load switch. This proved unsatisfactory owing to the bounce of relay contacts at time intervals shorter than 14 milliseconds. This was regarded as too restrictive of measurement, and recourse was made to complete electronic circuitry. After extended circuit trials using a Parabam pulse generator, it was decided that the limitations imposed by any commercially available unit were too restrictive in so far as the frequency range only extended to 2000 cps and the duty cycle from 20 to 80%. The circuit described in figure 1 was then developed to cover our particular requirement and should be of significant interest to others making similar measurements in this field and in the general field of electrochemistry. The unit comprises a pulse generator variable between 1 cps and 10,000 cps or higher with a primary duty cycle of 10 to 90%. This duty cycle is then extended by counter circuits so that its final range, obtainable by switching, is from 0.1 to 99.9%. Performance is highly satisfactory and the load circuit indicated permits operation to approximately 3 amps total (readily increased to 10 amps) with provision for reference electrode measurements during the off-duty cycle under essentially open-circuit conditions (10^{10} ohms, approximately). Provision is included for measurement on a Varian recorder under slower operating conditions and for oscilloscope presentation at higher pulse rates. The unit is now working satisfactorily in all major particulars.

Galvanostatic Measurements

In the absence of any commercially available equipment which would be regarded as suitable for our purposes, a precision galvanostatic circuit has been developed in these laboratories and is shown in figure 2. This unit possesses a stability of approximately 1 part in 20,000 over a total current range of 10 microamps to 50 milliamps. It is intended to extend this to 300 ma in the near future. A helipot control permits the establishment of any exact current within this range which is metered internally while the voltage fluctuations across the electrochemical cell system are observed externally by Varian recorder or oscilloscope.

Using a constant current technique, the change in potential of several electrodes was studied as a function of time. A porous nickel electrode (Clevite #3) was immersed in a freshly prepared 30% solution of KOH which had been boiled and cooled in a nitrogen atmosphere to eliminate dissolved oxygen. A constant current generator was connected between this electrode and a platinum gauze counter electrode, and a constant current of 10 ma was passed through the cell. The potential between the electrode under study and an Hg-HgO (30% KOH) reference electrode was measured by means of a potential divider and Varian 10 mV recorder. The electrode was allowed to reach the hydrogen evolution potential; the direction of current flow was then reversed. When the oxygen evolution potential was reached, the current was again reversed and the potential of the electrode was allowed to fall to the hydrogen evolution potential. The time required to desorb and adsorb hydrogen and oxygen was noted along with the slope of the double layer region. The former is a measure of how well the electrode will sustain current

if placed in a fuel cell while the latter yields the capacitance of the electrical double layer.

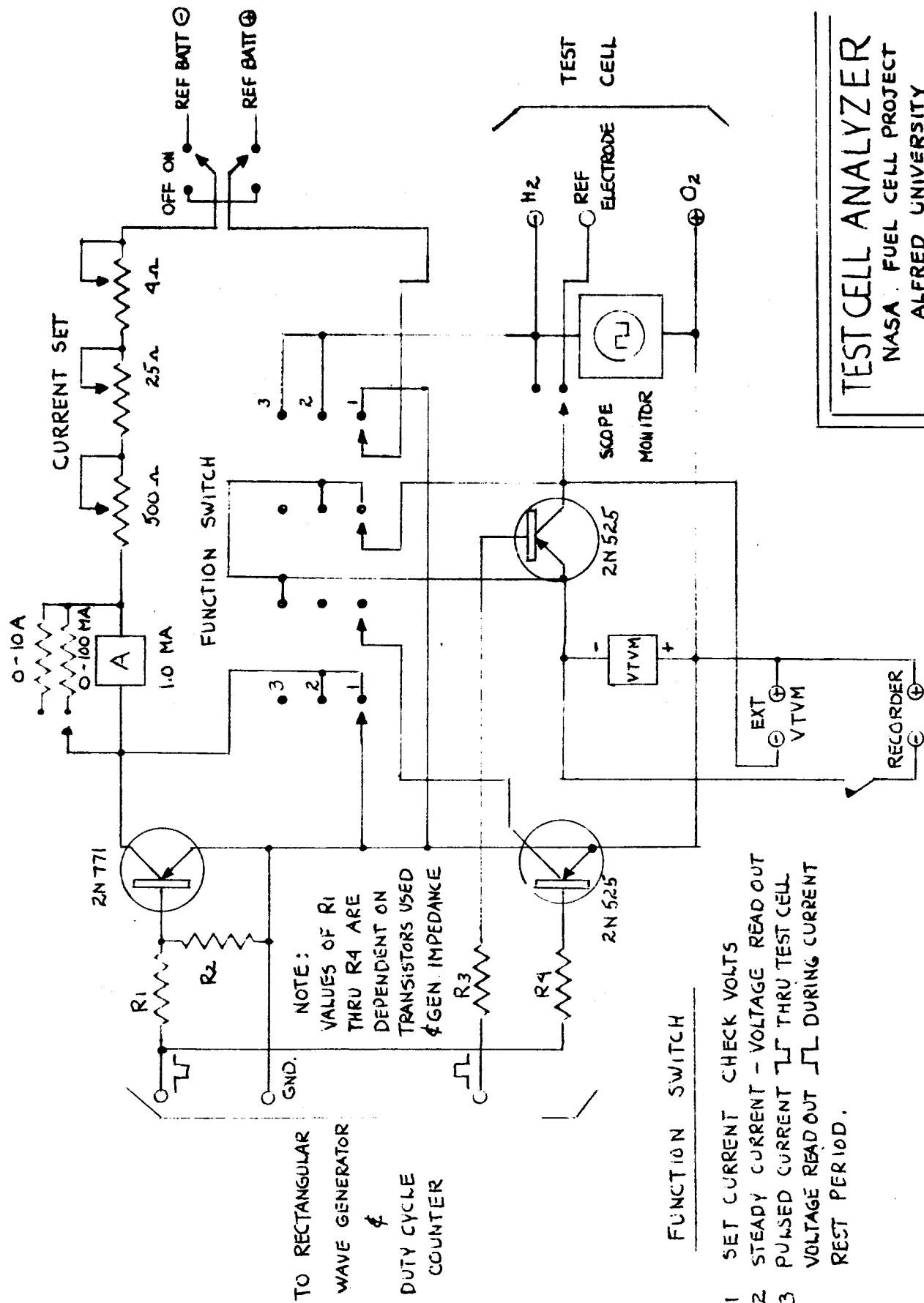
Nickel electrodes, 0.06 inch thick and 2 cm^2 in geometric area, manufactured by the Clevite Corporation, were first studied. Next, nickel electrodes of the same type and dimensions were platinized. The platinization technique included ultrasonic bathing in 3% chloroplatinic acid for 20 minutes, several rinsings in distilled water and electroplatinization at 100 ma/cm^2 for 5 minutes in another solution of the same strength. Studies indicate that with a constant impregnation time in the ultrasonic bath, the double layer capacity and, hence, the surface area of the platinized nickel electrode, does not increase significantly after approximately 5 minutes of platinization. Up to this time, the increase varies linearly with time. With constant platinization time, the double layer capacitance appears to increase linearly with an increase in impregnation time in the ultrasonic bath. However, deterioration of the electrode appears after an extended period in the bath.

An appreciable difference was noted between the platinized and non-platinized electrodes in both the times of adsorption and desorption and the slope of the double layer region, as is shown in figures 3 and 4. An increase in the time of adsorption and desorption indicated that the polarization should be less when the electrode under study was employed as a fuel electrode. This was verified when both nickel and platinized nickel were used as fuel electrodes. The plain nickel electrode was able to support less than 10 ma/cm^2 . Beyond this point, extreme polarization was observed. The performance of the platinized nickel electrode is shown in figure 5. The increase in the double layer capacitance is indicative of an increase in the effective surface area of the electrode due to platinization.

A third group of electrodes was treated in a manner similar to the second, employing a solution 3% in platinum and 3% palladium chloride. A marked increase in adsorption and desorption time was observed indicating that this would be an even better fuel electrode than the platinum. This is shown in figure 6.

The platinum-palladium-treated electrodes were then employed in a fuel cell and the potential was measured as a function of current density. Results of this measurement are shown in figure 5.

Preliminary investigations are being conducted on the above electrodes using a constant voltage across the electrolysis cell used for the above galvanostatic studies and measuring the current passing through the electrode under study. Using this potentiostatic technique, it is hoped that the kinetics of the formation and destruction of the chemisorbed layers of gases can be studied.



TEST CELL ANALYZER
NASA FUEL CELL PROJECT
ALFRED UNIVERSITY
PROF. TJ GRAY PHD

FIGURE 1.

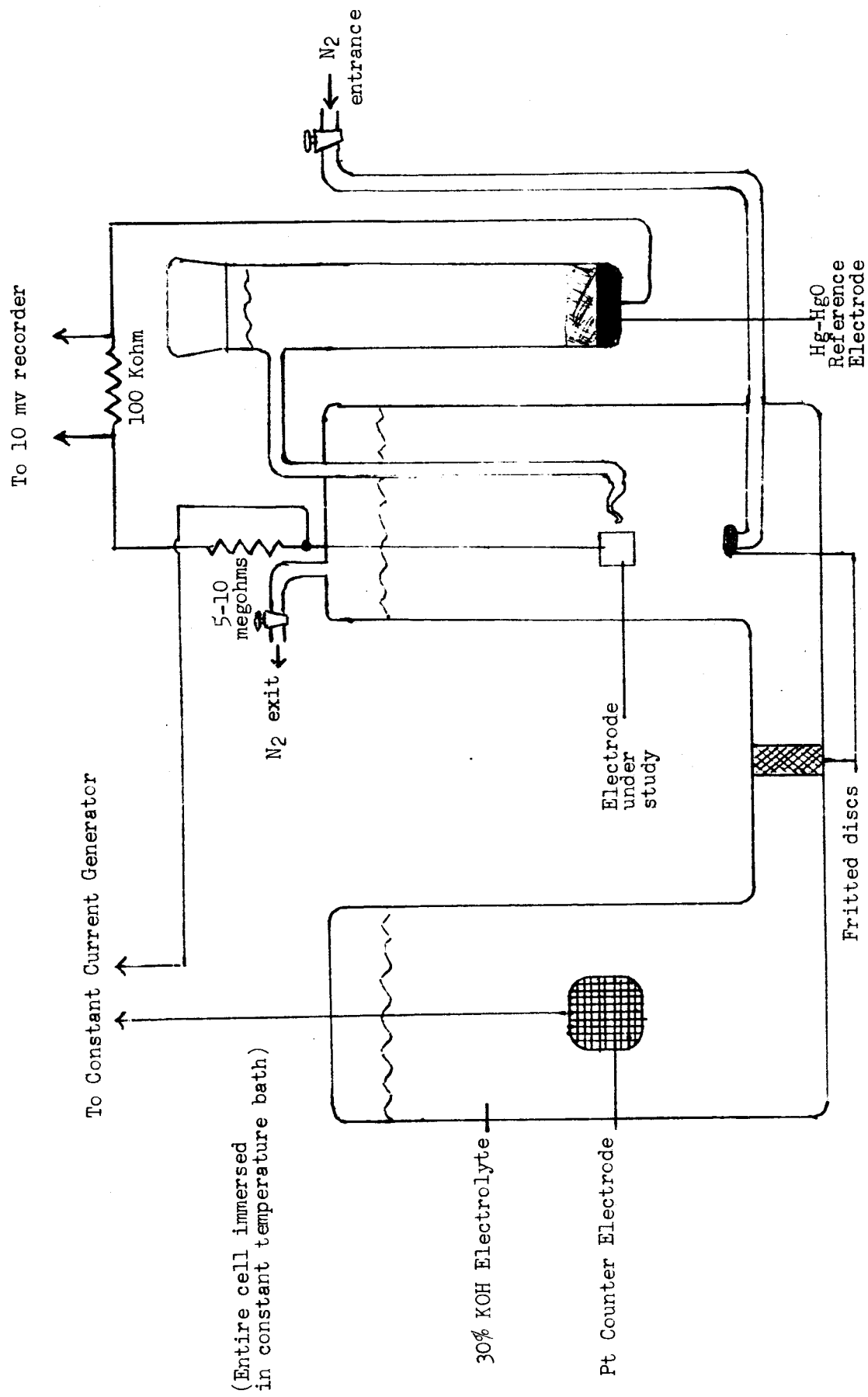


FIGURE 2a. Experimental Arrangement for Galvanostatic Measurements.

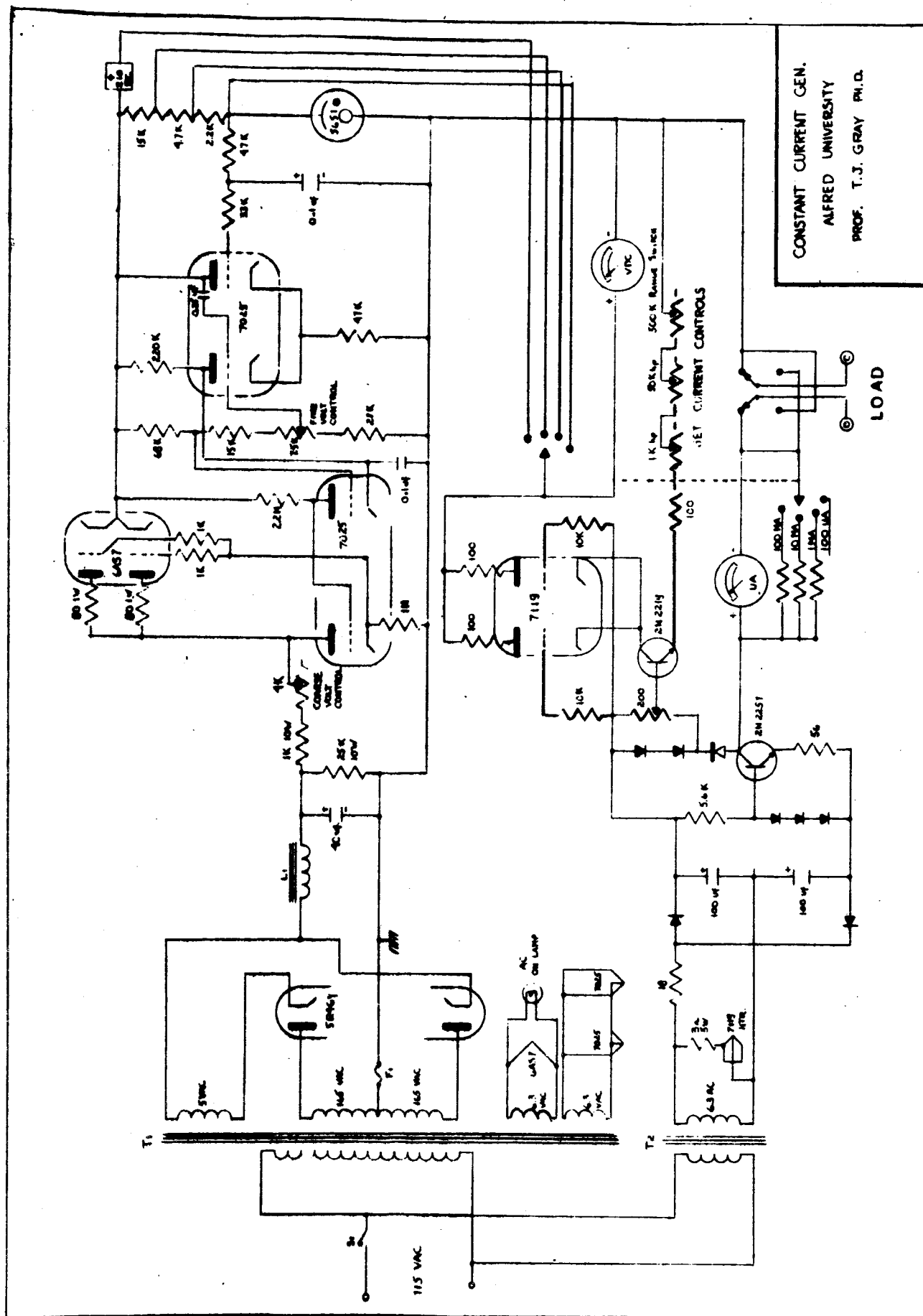


FIGURE 2b. Constant Current Generator Circuit.

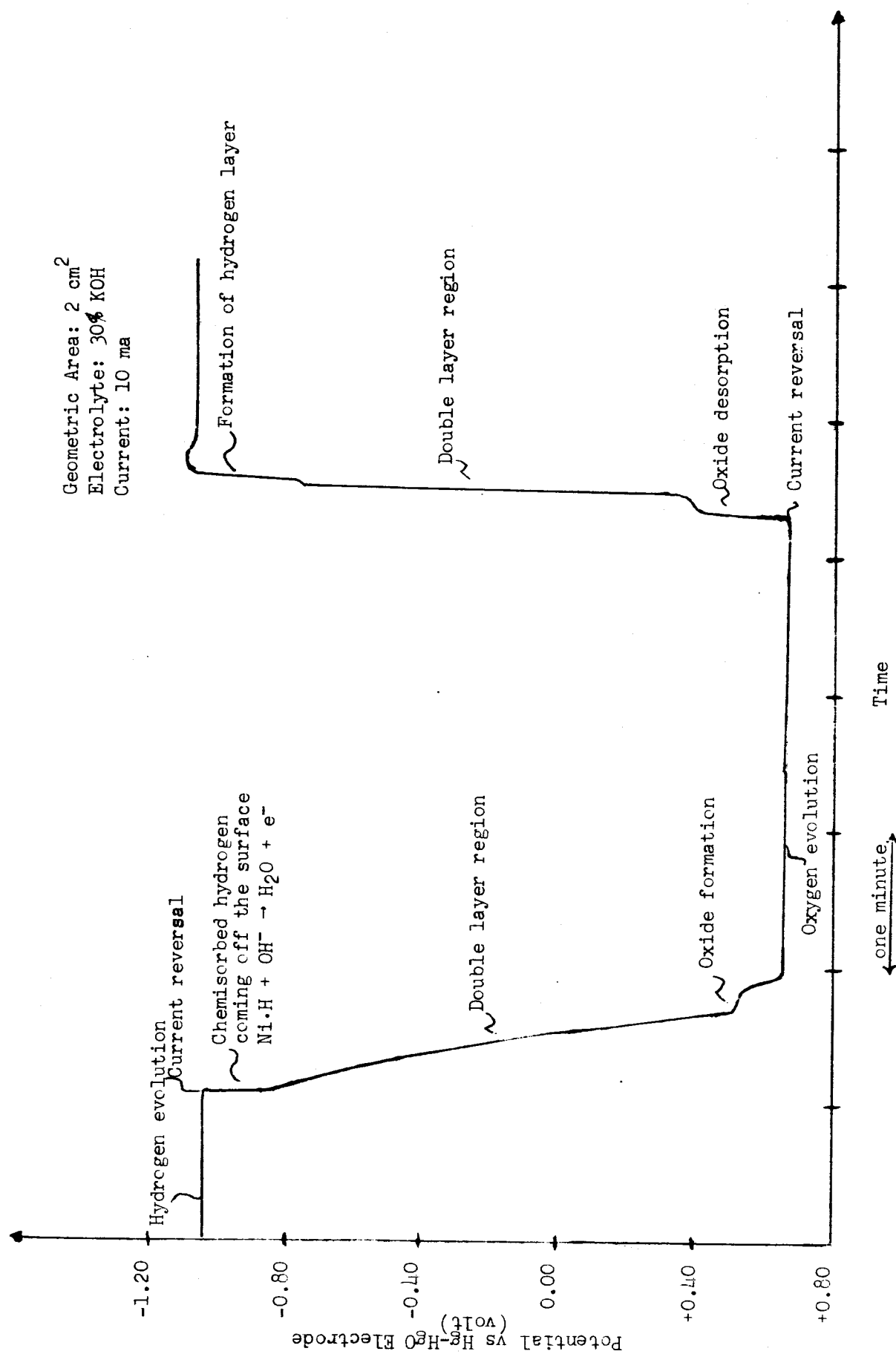


FIGURE 3. Galvanostatic Study of Nickel Electrode.

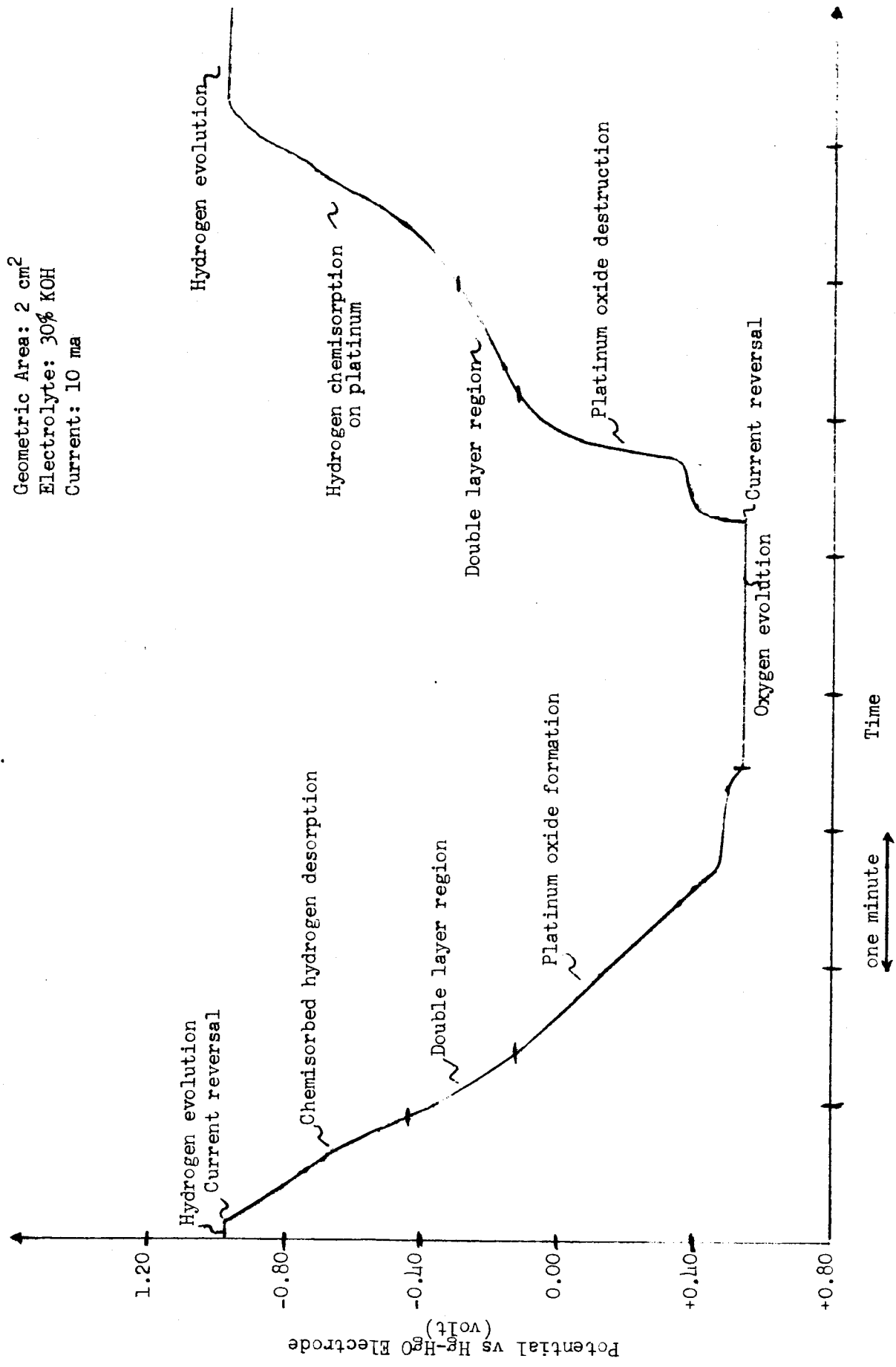


FIGURE 4 . Galvanostatic Study of Platinum Impregnated Nickel Electrode.

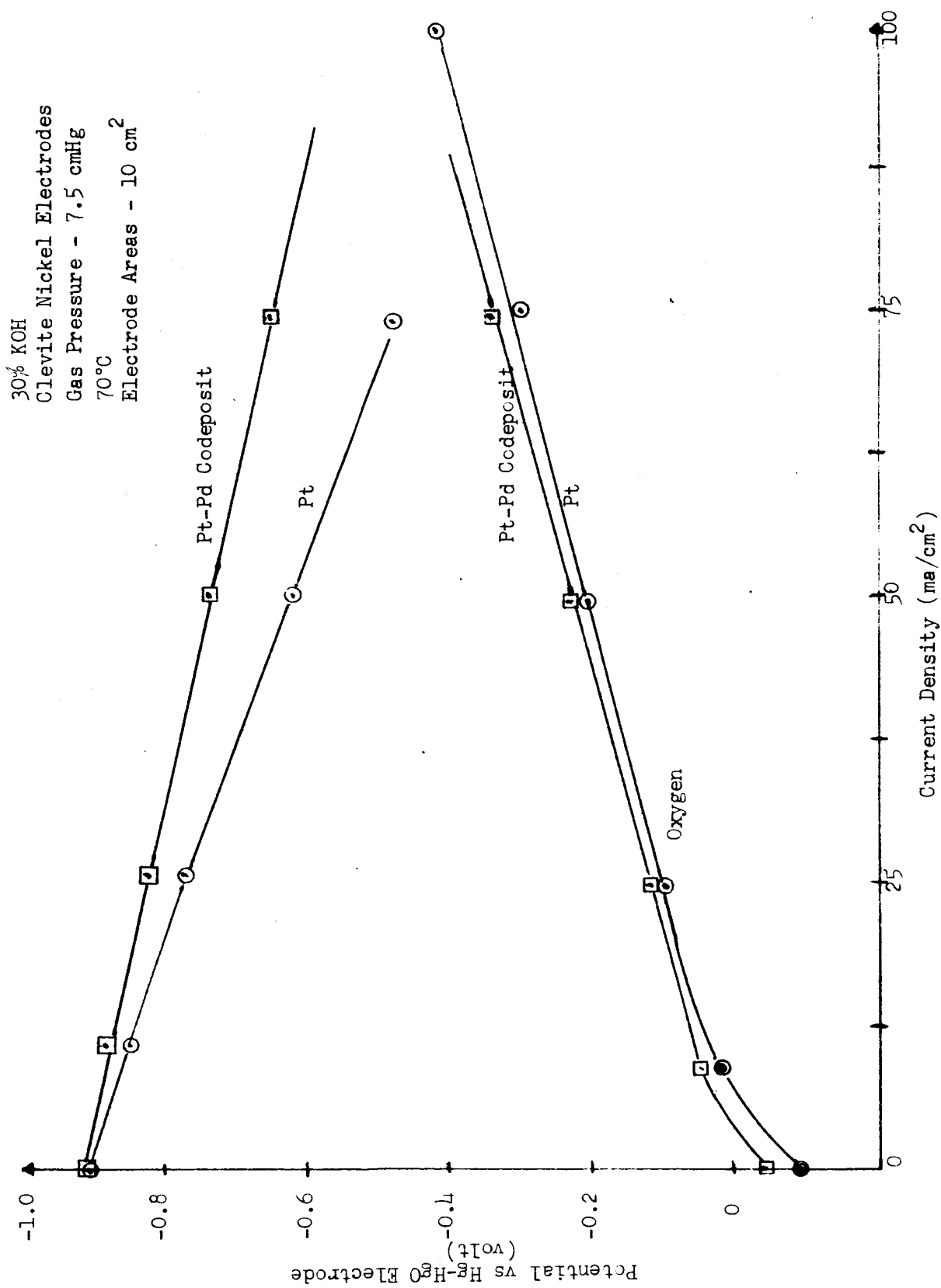


FIGURE 5. Fuel Cell Electrode Performances.

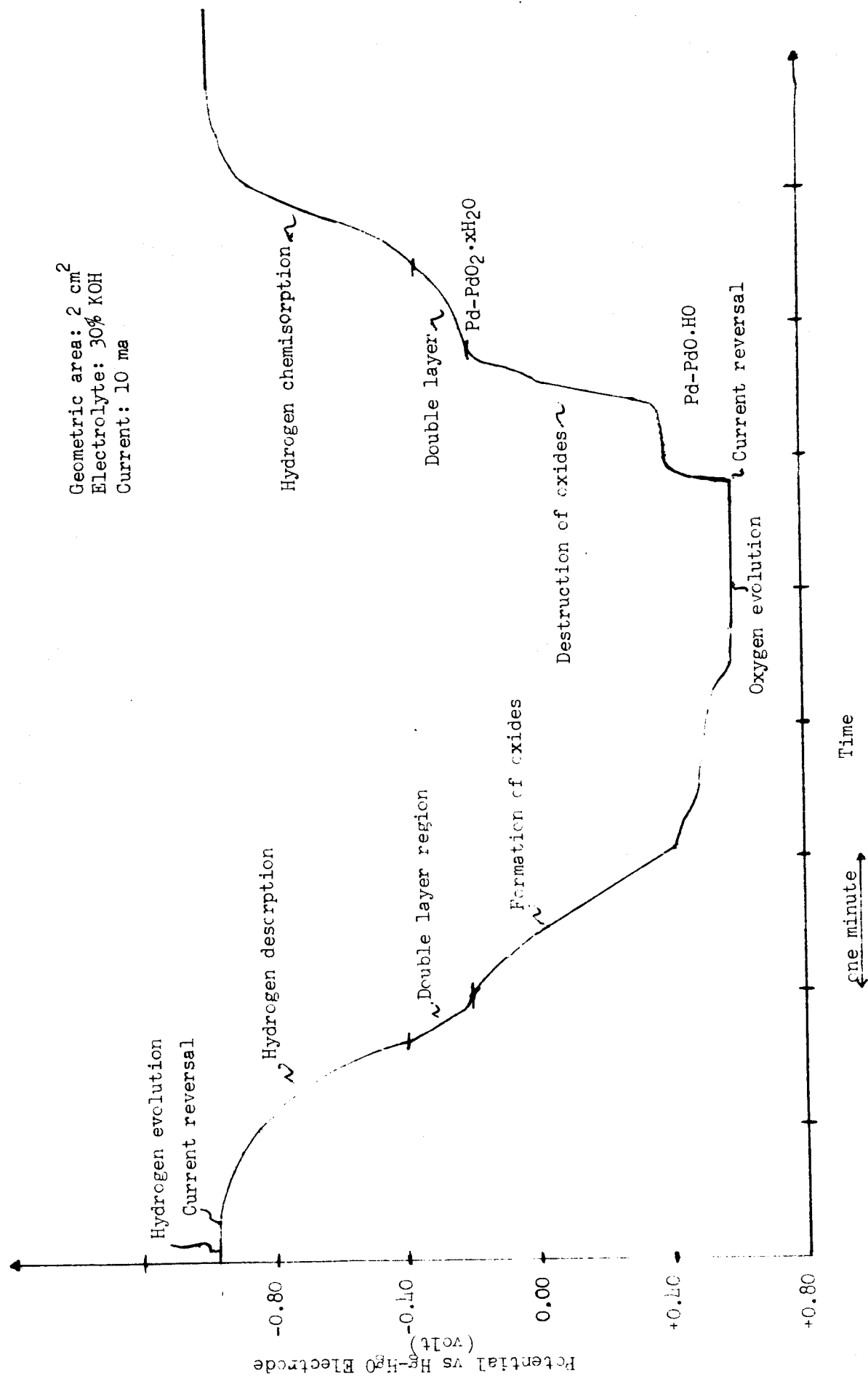


FIGURE 6. Galvanostatic Study of Nickel Electrode Impregnated with Platinum-Palladium Codeposit.